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First-Principles Band Calculation of TiO₂ with Brookite Structure

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Received April 1, 2004 ; Accepted July 5, 2004

The electronic structure of TiO₂ with brookite structure is calculated within the framework of the density functional theory (DFT). Calculated lattice constants are in excellent agreement with experimental values. Brookite is predicted to be a material with a direct band gap at the Γ point. The valence band with the width *ca.* 4.8 eV is mainly constructed from O 2p orbitals, whereas the lower conduction band mainly Ti 3d orbitals.

Key Words : TiO₂, Brookite, Energy Band Calculation, DFT, FLAPW

1 Introduction

Titanium dioxide (TiO₂) and related compounds have attracted a great deal of attention from viewpoints of their extensive applications.^{1–3)} Three phases of TiO₂ are well known, *i.e.*, rutile, anatase, and brookite. In particular, photocatalysis of anatase has been studied actively for several decades. In contrast, a pure brookite is difficult to be synthesized, so that few properties of brookite have been clarified experimentally. In addition, theoretical considerations on brookite are also still unsatisfactory. For instance, the electronic structures of rutile, anatase and brookite were calculated by using the orthogonalized linear combination of atomic orbitals (OLCAO) method.⁴⁾ However, the calculated electronic structures were not in agreement with experimental results. There were fairly disagreements between electronic structures calculated by different methods for anatase TiO₂.⁵⁾ In the present paper, we calculate the electronic structures of brookite with theoretically optimized structure using the full-potential linearized augmented plane wave (FLAPW) method, which enables us accurate

electronic structures of oxides.

2 Calculation Method

We have preliminary optimized the lattice parameters and atomic positions of brookite by minimizing the total energy of *Pbca* structure by using CASTEP code,⁶⁾ which is an ab initio molecular dynamics program. Brookite has a space group of *Pbca*, and both of Ti and O atoms occupy the Wyckoff positions 8c.⁷⁾ The Kohn-Sham wave functions of valence electrons were expanded to a basis set of plane waves within specified cutoff energy ($E_{\text{cut}} = 340$ eV). Valence electrons were described by Vanderbilt-type nonlocal ultra-soft pseudopotentials while tightly bound core electrons were ignored.⁸⁾ The exchange and correlation interactions were treated within the framework of the generalized gradient approximation (GGA), which is superior to the local density approximation (LDA).⁹⁾ The k-space integration over the first Brillouin zone was carried out at finite k-points (16 points) for brookite.¹⁰⁾ Table 1 lists the lattice parameters and atomic fractional coordinates calculated with CASTEP at

Table 1 Calculated parameters and coordinates of the atoms in brookite using CASTEP.

		Lattice parameters					
		a/nm	b/nm	c/nm			
Calculated		0.9278	0.5513	0.5161			
Experimental ⁷⁾		0.9184	0.5447	0.5145			
Atom	Wyckoff site	Calculated coordinates			Experimental coordinates ⁷⁾		
		x	y	z	x	y	z
Ti	8c	0.1292	0.0881	0.8623	0.1290	0.0972	0.8629
O(1)	8c	0.0104	0.1481	0.1824	0.0101	0.1486	0.1824
O(2)	8c	0.2296	0.1087	0.5360	0.2304	0.1130	0.5371

Fig. 1 Band structure of brookite along the high symmetry lines of the first Brillouin zone.

the DFT-GGA level of brookite together with those of the experimental values.⁷⁾ It is noticeable that theoretical lattice parameters are in excellent agreement with the experimental ones with a difference of *ca.* 1%. Using these data of lattice parameters and atomic positions, we calculated the electronic structure of brookite.

The energy band structure and density of states of brookite were obtained by the full-potential linearized augmented plane-wave (FLAPW) method, which has the highest accuracy in all of the *ab initio* band calculation techniques.¹¹⁾ Exchange and correlation are treated within the framework of the GGA.⁹⁾ Two types of the basis functions; a linear combination of (1) radial functions multiplied by spherical harmonics inside the muffin-tin (MT) spheres and (2) plane wave in the interstitial region were employed in this calculation. The MT spheres radii (R_{MT}) of the Ti and O atoms were 1.8 and 1.6 a.u., respectively, and 2600 plane waves were adapted. The plane wave cutoff was $R_{MT} \cdot K_{max} = 7.0$ and the k-point sampling was chosen to be 24 irreducible points within the first Brillouin zone (BZ). Further, we rotated the local coordinate system for Ti so that local axes are directed to surrounding oxygen atoms, approximately. Such rotation enables us to facilitate a theoretical analysis, because brookite consists of TiO_6 polyhedron in-

Fig. 2 Calculated density of states (DOS) of brookite.

clined to the crystallographic axis.

3 Results and Discussion

The calculated self-consistent band structure is shown in Fig. 1, along the high-symmetry directions of the irreducible BZ. The energy scale is eV and the origin of energy was arbitrarily set to be at the valence band maximum (VBM). A direct band gap at a Γ point is estimated to be 2.4 eV. We also evaluated the band gaps of rutile and anatase as 1.9 eV and 2.2 eV respectively. It should be noted that the band gap of brookite is slightly larger than those of rutile and anatase. The experimental values of the band gaps for rutile and anatase were reported to be 3.0 eV and 3.2 eV, respectively.^{12,13)} Similarly, the band gap of 3.4 eV was experimentally estimated for brookite nanoparticles dispersed in water.¹⁴⁾ The order of calculated band gaps for three phases of TiO_2 conforms well to the experimental results, although LDA cannot estimate an exact band gap, because the discontinuity in the exchange-correlation potential is not taken into account within the framework of density functional theory. Figure 2 shows the total density of states (TDOS) and local density of states (LDOS), corresponding to the energy region in Fig. 1. The lower valence band is comprised of O 2s orbitals lying in the range of -17.7 to -15.9 eV. The upper valence band in the range from -4.8 to 0 eV consists of O 2p orbitals hybridized with Ti 3d orbitals. The upper valence-band width of brookite is

Table 2 Structural data of brookite, anatase and rutile.

	Brookite ⁷⁾	Anatase ¹⁵⁾	Rutile ¹⁶⁾
Crystal system	Orthorhombic	Tetragonal	Tetragonal
Space group	<i>Pbca</i>	<i>I4₁/amd</i>	<i>P4₂/mnm</i>
Lattice constants (nm)	a = 0.9184 b = 0.5447 c = 0.5145	a = 0.3785 c = 0.9514	a = 0.4594 c = 0.2959
Volume/molecule (10^{-3} nm ³)	32.17	34.08	31.22
Bond length of Ti-O (nm)	0.187-0.204	0.1934 0.1979	0.1948 0.1980
Bond angle of O-Ti-O	77.3-104.7°	78.1°, 101.9° 92.5°	90.0° 81.2°, 98.8°

Fig. 3 Imaginary parts (solid line) and real parts (dotted line) of calculated dielectric functions for Cartesian components of brookite.

closer to that of anatase (4.5 eV) rather than rutile (5.5 eV). This is also expected from the similarity of the local crystal environment between brookite and anatase as listed in Table 2. On the other hand, the conduction bands below 7.6 eV are mainly composed of the Ti 3d orbitals. In general, Ti 3d orbitals are divided into two distinct structures, t_{2g} states (d_{xy} , d_{xz} , d_{yz}) and e_g states ($d_{x^2-y^2}$, d_z^2), owing to the crystal field splitting in the octahedral TiO_6 environment. The energy states ranging from 2.4 to 4.7 eV and 5.0 to 7.6 eV are respectively attributed to the t_{2g} states and the e_g states as shown in Fig. 2. The conduction bands above 7.6 eV have a large curvature and mainly represent s and p character.

Figure 3 shows the imaginary part ϵ_2 of the theoretical dielectric function obtained by using the k-points within the irreducible Brillouin zone. The orthorhombic structure allows ϵ_2 to separate into three Cartesian components x, y, and z. The absorption edge of each component locates at ca. 2.4 eV, originating from the interband

transitions between the VBM and the conduction band minimum (CBM). This value is well consistent with its corresponding direct gap at Γ point. ϵ_2 curves are divided into two energy regions from 2.4 to 5.8 eV and above 5.8 eV. The peaks in the lower energy region reflect to the transition from the valence band to the t_{2g} states and the one in the higher energy region to the valence band to e_g states, as expected from DOS analysis.

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